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Examination of the Corrosion and Salt Contamination of Structural Metal From the USS TECUMSEH

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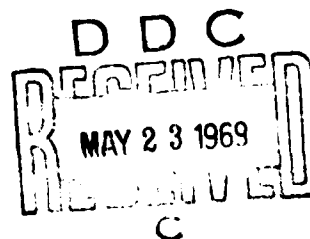
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ABSTRACT

The USS Tecumseh, sunk during the Civil War battle of Mobile Bay, is to be raised by the National Armed Forces Museum. Structural specimens have been studied by NRL to determine the effectiveness of various methods of removing seawater salts from the corroded metal. The nature of the scale deposits and the extent of corrosion were also studied. With the exception of the rivets, the wrought iron of the hull was found to be in surprisingly good condition. The peened ends of the rivets had been deeply attacked, and cast iron deck plates had been perforated in places. Hull joints had been penetrated by corrosion and seawater. Ultrasonic cleaning was found to be ineffective in removing the salts due to their encapsulation by the scale. Sandblasting to remove the scale, followed by flushing with water, appears to be the best cleaning technique. Analysis and examinations of the scale showed that there were typically 3 distinct layers, 2 of iron oxides and an exterior calcareous accretion. The formation of the scale layers can be explained by accepted corrosion mechanisms.

PROBLEM STATUS

This is a final report on this phase of the problem. Work on other phases of the problem is continuing.

AUTHORIZATION

NRL Problem C02-12
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EXAMINATION OF THE CORROSION AND SALT
CONTAMINATION OF STRUCTURAL METAL
FROM THE USS TECUMSEH

INTRODUCTION

At the request of the National Armed Forces Museum of the Smithsonian Institution, Code 6170 of NRL (Surface Chemistry Branch) has participated in the discussion of corrosion problems associated with the planned recovery of the USS Tecumseh, a monitor sunk in the entrance to Mobile Bay during the Civil War. The recovery offers a unique opportunity to view at first hand the results of a hundred-year exposure of ferrous metals to the corrosive environment of a tidal estuary. The Corrosion Section of the Surface Chemistry Branch has examined typical metal sections from the ship's structure and explored the possible utility of ultrasonic cleaning techniques for the removal of salt and salt solutions from corroded surfaces and structures. This report summarizes the findings from that study.

STRUCTURAL METAL SPECIMENS

The specimens brought up by divers for study were a portion of a blower housing, two pieces of cast iron engine room deck plate, and of greatest interest, a section of the hull including hull plating and a portion of a transverse frame. This ship was not of ironclad construction. Although some wood was used in its construction, the hull was built principally of wrought iron plates 1/2 inch thick joined by rivetting. The hull specimen was cut from the "B" strake on the starboard side near frame 42. Roughly 60 x 40 cm in size, it consisted of exterior hull plating, a spacer, and frame plate fastened to 9 cm angle iron by 6 rivets (Fig. 1). The specimens of deck plate were taken from the same location. The hull specimen and the deck plate were selected for careful study as being of particular interest and generally representative of the condition of all the iron structure and objects in the ship. The hull specimen and the large piece of deck plate were sectioned with a bandsaw into manageable pieces for laboratory examination.

CONDITION OF THE METAL

The wrought iron was generally in unexpectedly good condition. The surfaces on the interior of the hull were pitted no more deeply than about 1.5 mm, and the oxide layers in the scale averaged only 1 or 2 mm. The exterior of the hull plating was more deeply corroded due to the lack of a protective scale coating and, probably, to the greater concentration of oxygen and greater velocity of flow in the water outside the hull. This surface was corroded in the wood-grain pattern typical of wrought iron, with a maximum relief depth of 2.5 mm (Fig. 2). The remaining thickness

of the metal varied from 9 to 12 mm (0.35 to 0.47 in.). The depth of the corrosion may be two or three times as great near the mud line (1). This possibility should be checked for by drilling a few holes in the hull in this area. A polished section of the hull plating showed numerous slag inclusions, flattened and aligned by the rolling process. Some were several inches long in the fore-and-aft direction. The frame plate contained a crack or planar inclusion extending 2 1/2 in. from the lower edge and several inches in length. It might have been formed by the enfolding of the billet surface during working. The cast iron engine room deck plate specimen was more severely corroded. The metal was perforated in places, and had a maximum thickness (exclusive of the rim) of 8 mm (0.3 in.). Judging from the oxide layer, the original minimum thickness may have been 9 mm (0.35 in.). An appreciable fraction of the metal is composed of inclusions, many as large as 0.1 mm. These are not flattened or oriented, which confirms that the deck plates were cast (Fig. 3).

CONDITION OF THE JOINTS AND RIVETS

The faying surfaces of the hull plates, angles, and frames were to have been coated with white lead and oil when the ship was constructed. When the specimens were sectioned and dismantled only traces of this material could be seen. Some joints were full of solid matter, while others had gaps of up to 2 mm. All had been penetrated by saltwater. The rivets were not corroded unusually on their head ends, but the upset ends were deeply pitted (Figs. 4 and 5). The rivets in the hull plating were the most deeply pitted. The oxide wedged within the remaining metal might help to prevent the rivets from pulling through. After sandblasting, however, they look as though they might easily collapse and pull through under tension. It may be necessary to restore the rivets by welding or perhaps by the application of a glass-filled epoxy resin.

Apparently the peening of the rivets opened up the metal along the planes of inclusions, enabling corrosion to penetrate more rapidly because of the increased surface area. Since the corrosive medium was attacking the rivets from the ends, in the same direction as the slag inclusions ran, the inclusions were unable to block the penetration. Uhlig (2) states that the corrosion rate of wrought iron in seawater should be the same as that of other iron alloys. This may be true for modern wrought iron, but does not appear to be true for these old specimens with their extensive slag inclusions. The deeply sculptured surfaces and rivet ends testify to the operation of a localized protective effect. Although this local protection may have accelerated the pitting in unprotected areas, even the deepest penetration appears to be only half the depth of the corrosion on the cast deck plate. The picture is complicated, however, by the very long exposure and the resulting calcareous deposits on the metal surfaces.

REMOVAL OF SALTS

The presence of chlorides in the specimens was detected and located by the use of silver nitrate paper. Cut surfaces to be examined were washed briefly with distilled water to remove some of the debris distributed across the surface by the saw blade. Fine filter paper moistened with silver nitrate solution was then pressed onto the moist surface. The chloride ions dissolved from the specimen reacted with the silver nitrate to form an insoluble silver chloride imprint on the paper. After the paper had been washed several times in distilled water to remove the excess silver nitrate, sodium sulfide solution was applied to blacken the silver chloride deposits and make the imprint more visible. The hull plate and frame assembly joints were found to have been permeated with salts. The gap between the frame and the angle iron was particularly rich in chlorides. The corrosion deposits, although dense on the exterior were frequently microporous or even penetrated by microscopic channels beneath the surface. A section of this specimen was immersed in a detergent solution with ultrasonic agitation for 30 min. The cut ends had been sealed to prevent access by the cleaning solution through this route. When a slice was cut from this section the chloride concentration in the freshly exposed joints was found to be as great as before. This section was then descaled by sand-blasting by Armed Forces Museum personnel and again subjected to ultrasonic cleaning. Chlorides were still found in the joints. The nearly impermeable scale deposits at the edges of the joints prevent the circulation of the cleaning solution through the interior voids. Much of the salt is probably also encapsulated in the rust and scale and is not readily extractable. To gain access to the joints for effective ultrasonic cleaning it would be necessary to apply an inhibited acid to dissolve the scale. In cold 50 % hydrochloric acid the calcareous portion of the scale dissolves readily. The iron oxides dissolve upon heating. Considering the magnitude of the task and the hazards involved, however, the use of acid does not seem practical.

The exterior surface of the hull plating was also examined for the presence of chlorides after various cleaning methods had been applied. One area was sandblasted (at NRL) so that all scale was removed except for small amounts protected by overlying metal. The surface was then tested for chlorides without washing. The concentration was found to be heavy, particularly in the vicinity of the remaining scale. Another similar sand-blasted area was washed under running tap water for 5 min. The chloride concentration was much lower than before and again concentrated near the scale. The section which had been sandblasted and ultrasonically cleaned was found to have only traces of chloride remaining.

The application of ultrasonic cleaning techniques to the hull of the ship would help in the removal of the accessible salt, but probably would not be worth the effort and expense. It appears that the best cleaning technique would be similar to that already contemplated:

- 1) Removal of mud and loose scale by high-pressure water or steam
- 2) Chipping and thorough sandblasting to remove the scale completely
- 3) Prolonged washing (an hour or more) with fresh water or steam to leach out the remaining salts.

The surface should then be coated with a chromate, zinc, or lead oxide primer when thoroughly dry. The salt not removed by this procedure probably could be well enough sealed off from the atmosphere that it would be harmless.

PHYSICAL CHARACTERISTICS OF THE SCALE

The scale formations on the wrought iron surfaces inside the hull (Fig. 6) were from 1.8 to 10 mm thick, with an average thickness of about 3.4 mm. Adhering to the metal was a red-brown layer of variable thickness (0.1 - 2 mm). Some harder black and white inclusions were seen in this layer. The second layer (Fig. 7) was of variable thickness, but was usually thicker than the first. This layer was porous and weak, generally black with red and white inclusions. The white inclusions were crystalline; the red ones amorphous. Numerous bubbles were present, some with crimson linings. When the scale was broken from the metal, the fracture generally occurred between these first two layers. In some cases the black material was seen to change to red-brown after being exposed to the atmosphere, as the iron was oxidized further to ferric oxide. The outermost layer (Fig. 7) was very hard, uniformly 1.2 mm thick, and all black and white with the outer 0.05 mm being white. To determine the nature of the pitting the scale on one area was broken from the metal which was then sandblasted. There did not seem to be any correlation between the extent of pitting and the thickness of the overlying scale. Nevertheless, the appearance of the scale layers suggests that: 1) the boundary between the first two layers approximates the original surface of the metal, 2) the middle layer grew outward from the surface as corrosion proceeded, and 3) the outer calcareous layer deposited by accretion from the water.

In the 1/2-inch gap between the edge of the frame and the interior of the hull plate, a collection of debris was found encapsulated by scale and impregnated with iron compounds. Included in this material were some unidentified fibers and a few pieces of wood sawdust, which probably fell into the bilge during construction of the ship and lodged in the crevice.

The scale formed on the cast deck plate (Fig. 8) was in layers similar to that on the wrought iron. The inner layer was a strong but brittle material which is formed by the graphitic corrosion (3) of gray cast iron. The original shape of the metal was preserved in the outline of this layer. On the upper surface of the deck plate (facing downward in the sunken hull) the outer layers of scale were nodular in form, with the middle layer weaker and more porous than the corresponding layer on the wrought iron. The maximum thickness was about 15 mm. On the lower side of the plate (facing upward in the sunken hull) the deposit was 2 - 8 mm thick and lacked the black and white calcareous external layer. It was relatively dense and hard, variegated red, brown, and black, and appeared to contain biological remains.

CHEMICAL CHARACTERISTICS OF THE SCALE

Portions of the scale were subjected to spectrochemical and wet chemical analyses to determine their composition. The outer two layers of scale from the wrought iron were partially separated by chipping and scraping. It was possible to obtain a relatively pure sample of the middle layer, but the exterior layer could not be well segregated. It was therefore necessary to determine its composition by difference between the combined and the middle layer analyses. The spectrochemical analyses are given in Table 1.

TABLE 1

Spectrochemical Analyses of Wrought Iron Scale

Amount, %	Middle Layer	Partially Segregated Exterior Layer
10-100	Fe	Fe Ca
1.0-10		Mg Al
0.1-1	Si Ca Al Zn Mg	Si

TABLE 1 (Continued)

Spectrochemical Analyses of Wrought Iron Scale

Amount, %	Middle Layer	Partially Segregated Exterior Layer
< 0.1	Mo Cu Ti Ba	Mo Ti Ba Cu

Conventional gravimetric methods were used to determine quantitatively the composition of the scale. The results are given in Table 2.

TABLE 2

Results of Analyses

Wrought Iron Scale

	Middle Layer Only	Combined Middle and Exterior Layers
Free Water	Dried	2.0 %
Water solubles	3.6 %	3.6
Acid insolubles	3.6	7.2
Fe	51.8	32.6
Al	0.1	
Ca, Zn (as CaO_3)	1.1	
S	0.4	-

From these data it is possible to make some deductions about the molecular composition of the scale and to determine the composition of the exterior layer. The exterior layer was 1.2 mm thick and the average thickness of the sample scale was 3.3 mm. The average thickness of the middle layer was therefore 2.1 mm. Assuming equal density, the weight ratio was

$$\frac{\text{Middle}}{\text{Exterior}} = \frac{2.1}{1.2} = \frac{1.75}{1}$$

and the abundances can be calculated as follows:

$$\% \text{ Exterior} = 2.75 \times \% \text{ Combined} - 1.75 \times \% \text{ Middle}$$

The presence of iron as a hydrated magnetite was assumed as this material would be likely to form on submerged iron. The relatively strong attraction of the samples to a magnet supported this assumption. Other iron oxides were undoubtedly also present in smaller quantities. The probable composition of the scale is given in Table 3.

TABLE 3

Probable Composition

Wrought Iron Scale

	Middle Layer	Exterior Layer	Combined Layers
$\text{Fe}_3\text{O}_4 \cdot 4\text{H}_2\text{O}$	92.6%	2%	60.3%
FeS	1.1		
Al_2O_3	0.1		
$\text{CaCO}_3, \text{Zn}^{++}$ (As CaCO_3)	1.1	79	29.3
SiO_2 , Silicates, Organics	3.6	14	7.3
NaCl, MgCl_2 , CaCl_2 , KCl	3.6	4	3.7
	102.1	99	100.6

The analyses support the observation that the middle layer grew out from the surface while the exterior layer was deposited from the water. The middle layer consisted almost entirely of iron oxide with a minor amount of silicates, some of which might have come from the slag in the metal. The exterior layer was calcium carbonate (limestone) containing some finely divided silica and silicates from the water. Water-soluble salts were evenly distributed through both layers. The amount of silica in the calcareous outer layer of the scale is interesting in the light of the fact

that it was prominent in scale formed on interior surfaces that were facing downward into what should have been almost completely stagnant water. The silica content must have been deposited from a highly colloidal non-settling state, either because of electrical neutralization by multivalent iron ions from the scale, or by an electrophoretic process associated with corrosion currents.

The scale from the deck plate appeared to be similar to that from the wrought iron in elemental composition (Table 4).

TABLE 4
Spectrochemical Analyses of Cast Deck Plate Scale

Amount, %	Inner Oxide Layer	Combined Middle and Exterior Layers
10-100	Fe	Fe Ca
1.0-10	Si	Mg
0.1-1	Mn Ni	Mn Si Al
< 0.1	Al, Mg Cr, V Cu, Ti Co, Ca	Ti V Cu

The silicon content of the oxide layer was high due to the high slag content of the metal. The calcium and magnesium contents were very low, indicating that there was little diffusion of salts into this layer.

MECHANISM OF SCALE FORMATION

The observed characteristics of the scale are compatible with the corrosion mechanisms described by Evans (4). Figure 9 is a schematic representation of a porous oxide layer, in contact with the metal, and permeated with seawater. The oxide is cathodic to the metal, so that a galvanic corrosion cell is formed. Ferrous chloride is formed at the metal surface and sodium hydroxide at the oxide surface. These come together and form ferrous hydroxide which is further oxidized by oxygen diffusing into the scale. The oxides thus are formed within the scale, causing it to grow outward from the region in which the mobile ferrous ions and hydroxyl ions meet to form the insoluble ferrous hydroxide. This region is apparently in the middle scale layer. The rate at which the corrosion proceeds is controlled by the rate at which oxygen diffuses into the scale from the

surrounding water. Meanwhile, the slight alkalinity in the scale causes calcium carbonate to deposit forming the exterior layer. This dense layer ultimately limits the diffusion of oxygen into the scale and virtually halts the corrosion of the metal over which it lies.

CONCLUSIONS

1. In the parts examined, the exterior peened down ends of the rivets connecting the hull plate to the angle iron (and thus to the frame) were seriously penetrated by corrosion. It seems possible that some of these ends may collapse and pull through the rivet holes under stress if they are not strengthened.

2. The spaces or crevices between members of riveted joints were usually filled with microporous corrosion products which in turn were saturated with seawater.

3. Neither fresh water flushing nor ultrasonic washing will effectively remove chloride from deep pockets of corrosion products. Ultrasonic cleaning may reduce the chloride content of thin layers or shallow pockets of corrosion scale to safe levels, but the gains from applying ultrasonic cleaning to major surfaces such as the hull do not appear commensurate with the difficulties involved. In the cleaning of small items removed from the ship, the use of ultrasonic cleaning in conjunction with other techniques still appears advantageous.

4. The best technique for cleaning and preserving the hull appears to be:

- 1) Removal of mud and loose scale by high-pressure water or steam
- 2) Chipping and thorough sandblasting to remove the scale completely
- 3) Prolonged washing with fresh water or steam to leach out the remaining salts
- 4) Painting, with a corrosion inhibiting primer.

5. The scale consisted typically of three layers; an oxide layer preserving the original outlines of the metal, a porous oxide layer which grew out from the metal, and a hard calcareous accretion on the exterior. The formation of the scale layers can be explained by accepted electrochemical and oxidative corrosion mechanisms. The dense calcareous layer limited the corrosion of the metal over which it formed by reducing the diffusion of oxygen from the water into the oxide layers.

ACKNOWLEDGMENT

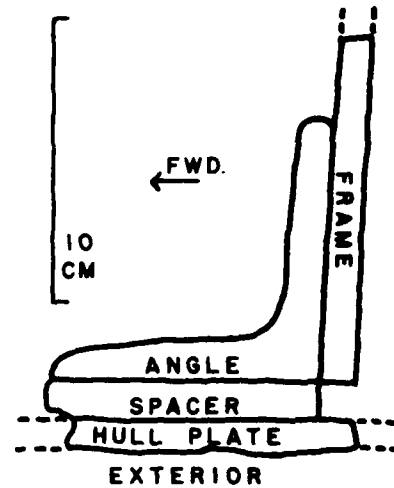
The spectrochemical analyses were performed by Mr. S. H. Cress of the NRL Metallurgy Division.

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3. Ibid., 105
4. U. R. Evans, in H. H. Uhlig, "The Corrosion Handbook," 4, Wiley, New York, 1948



(a)



(b)

Fig. 1 - Section of hull structure from the Tecumseh



Fig. 2 - Polished section perpendicular to the exterior surface of the hull plating showing pockets of corrosion near the surface and slag inclusions in the metal (section normal to the rolling direction)

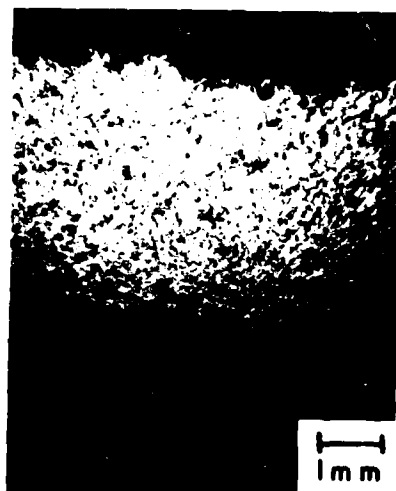


Fig. 3 - Polished section of cast iron deck plate and oxide layers showing inclusions in the metal (perpendicular to the plane of the plate, not etched)

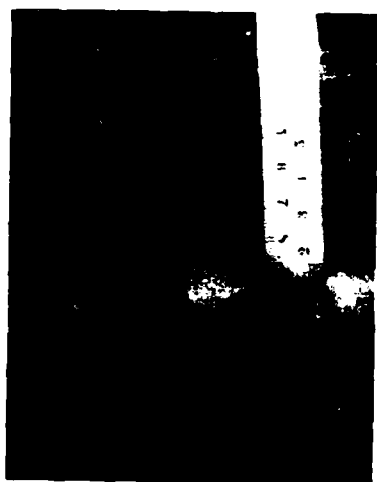


Fig. 4 - Head of rivet through angle, spacer, and hull plating (sandblasted, looking down on angle iron)



Fig. 5 - Peened end of rivet shown in Fig. 4 (sandblasted, also showing exterior surface of hull plating, fwd. to left)



Fig. 6 - Scale removed from the frame plate (aft side)

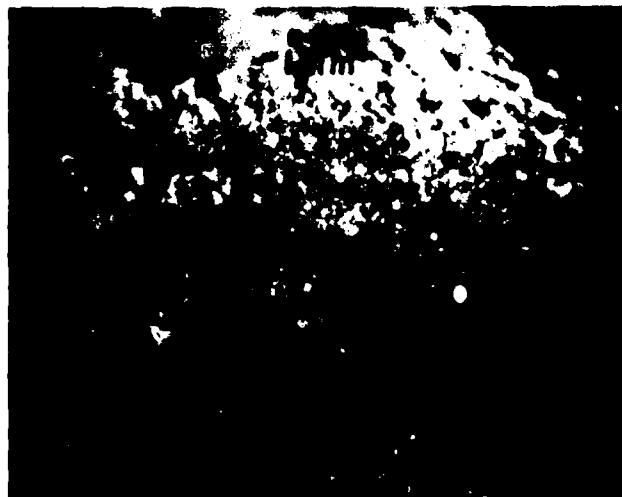
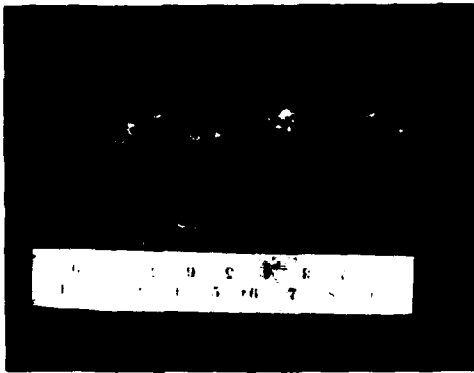
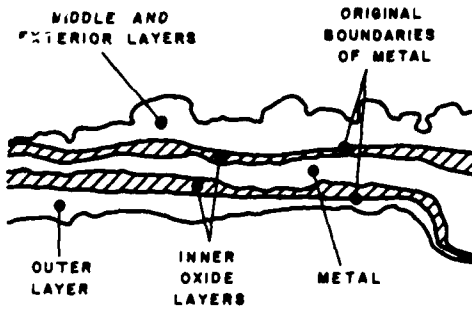


Fig. 7 - Surface of a fracture through the middle and exterior layers of scale on the angle iron (exterior surface at top)



(a)



(b)

Fig. 8 - Sawn section of deck plate, near the edge. The original lower surface of the plate was flat, except for the rim around the edge, while the upper surface had a pattern of raised dia -

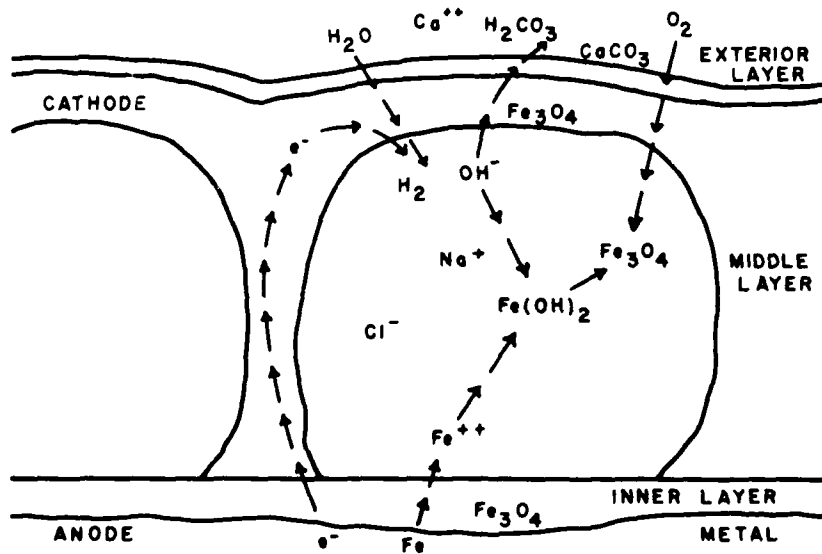


Fig. 9 - Scale-forming reactions

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